

Empirical Force Field and *Ab Initio* Calculations on Allyl Cations

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ABSTRACT

Allyl cation geometries optimized using an extended version of MMP2, newly parameterized for localized and delocalized classical cations, compare favorably with those obtained at the MP2(full)/6-31G* level. Hence, the force field should provide good starting structures for *ab initio* calculations. The π -electron densities obtained by these two very different methods are quite similar. The relative energies of various isomers at MP4/6-31G*//MP2(full)/6-31G* are reproduced well by the force-field calculations. The heats of formation calculated by MMP2, as well as those predicted from the *ab initio* data, agree with experimentally determined values. The force-field method provides interpretive capabilities. Energy differences between isomers can be separated into electronic and steric contributions, reasonable estimates of resonance energies are given, and nonbonded resonance energies in delocalized cations can be evaluated. The stabilizing 1-3 π -interactions in allyl cations are quite significant, but are reduced by alkyl groups hyperconjugatively and sterically. © 1997 by John Wiley & Sons, Inc.

Introduction

Attempts to apply empirical force-field computations to carbocations date back to the early days of such methods.¹ The original aim was to estimate strain energies, which could be correlated with rate constants of solvolysis reactions at bridgehead positions of various polycyclic systems.² In contrast to the early parameterization strategies, we have developed a new empirical

force-field method, which reproduces MP2(full)/6-31G* *ab initio* carbocation geometries with high accuracy.³ This method is based on Allinger's MMP2 program,⁴ which combines a SCF treatment of delocalized π -systems with an empirical force field. Consequently, π -electron densities and geometries for delocalized cations like allyl or benzyl can be obtained. Moreover, hyperconjugation effects introduced via a quantum-chemical term in Allinger's SCF routine also are given quite reasonably.³

The variations in allyl cation geometries are sensitive to the hyperconjugative interactions of alkyl substituents.⁵ Alkylated allyl cations were

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experimentally characterized by H-NMR, UV, and IR spectra.⁶ Olah and Mayr reported ¹³C-NMR spectra of alkylated allyl cations (e.g., formed by protonation of alkynes in magic acid solutions).⁷ Gas phase ion measurements provide heats of formation for a large number of allyl cations.⁸ The recent development of a matrix isolation technique for generating carbocations⁹ enabled the direct observation of small allyl cations with only a few stabilizing alkyl substituents. The parent allyl cation, the smallest long-living carbocation observed in a solid SbF₅ matrix,¹⁰ could be characterized by IR but not by NMR spectroscopy.¹¹

Combinations of theoretical and experimental methods led to further insights into allyl cation structures. Schleyer and coworkers gave the first extensive *ab initio* study of alkyl-substituted allyl cations with the minimal STO-3G basis set.¹² Wiberg and coworkers have recently reported results for some alkylated allyl cations using correlated *ab initio* methods at 6-31G* basis sets.⁵ Experimental ¹³C-NMR chemical shifts of allyl cations agree well with values obtained by applying the GIAO-MP2 method¹³ on MP2(full)/6-31G* optimized structures,¹¹ which proved clearly that these MP2(full)/6-31G* geometries are realistic.

Our force-field method not only reproduces the MP2(full)/6-31G* geometries, and does so rapidly, but also enables an analysis of nonbonded π -interactions and homoconjugation^{14,15} effects. Homoconjugation in carbocations was explored by Winstein and coworkers about 40 years ago.¹⁶ An extension of this concept to homoaromaticity^{17,18} was confirmed by experimental evidence.¹⁹ Olah and coworkers recognized the importance of nonbonded 1-3 π -interactions in the allyl cation three decades ago.⁶ Our force-field method is able to verify these early conclusions.¹⁴ When the allyl system is included in a four- or five-membered ring, the importance of these nonbonded π -interactions increases significantly, and homoaromatic cationic π -systems,²⁰ like the homocyclopropenyl cation, result.²¹

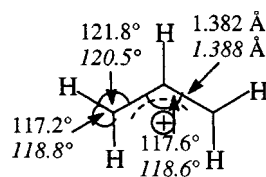
Methods

All *ab initio* calculations used the GAUSSIAN 92²² and GAUSSIAN 94²³ programs on Convex C220/384, Hewlett-Packard 9000-735, and Cray YMP-864 computers. The energies discussed in the text refer to single-point calculations on MP2(full)/6-31G*^{24,25} optimized geometries with

fourth-order Møller–Plesset correction including single, double, triple, and quadruple excitations (MP4sdtq)²⁶ for molecules up to six carbon atoms; the triple excitations were not included for larger molecules (MP4sdq).²⁶ All optimized structures were characterized by HF/6-31G*//HF/6-31G* frequency calculations and zero-point energies. π -Electron density matrix elements were obtained by applying NLMO/NPA analysis²⁷ on the MP2(full)/6-31G* structures using RHF/6-31G* wave functions. The force-field calculations were performed with the modified MMP2 program²⁸ adapted to the Convex C220/384 computer.

Parent Allyl Cation

The results for the geometry and the π -electron densities of the parent allyl cation **1** obtained by MMP2 and MP2(full)/6-31G* optimizations agree well.³ The MMP2 heat of formation, 225.0 kcal/mol, corresponds to the experimental value of 226 kcal/mol.²⁹



1 C_{2v}

italics: MMP2 values

The resonance energy of the allyl cation was calculated via the force-field method by comparing the π -energies of the allyl cation (calculated by the SCF routine of MMP2) and ethene, which also has two π -electrons, but has no corresponding resonance stabilization. Table I lists the MMP2 π -energies.

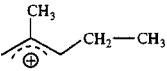


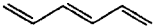
π -Bond energies can be obtained by different calculational³⁰ and experimental procedures.³¹ One common way is to equate the rotational barrier of a double bond with its π -bond energy,³² which gives a value of 65 kcal/mol for ethene. A different way is to compare the dissociation energies involving double (C=C) and single (C—C) bonds and to subtract the results.³³ The ethene π -bond energy obtained by this method is 87.2 kcal/mol.³¹ A third calculational procedure³¹ combines the difference of heats of hydrogenation of related double (CH₂=CH₂ to CH₃—CH₃) and single bonds (CH₃—CH₃ to 2 CH₄) obtained by isodesmic equations with bond dissociation energies

TABLE I.
MMP2 π -Energies (E_π), σ -Energies (E_σ), and Steric Energies (E_{st}) of some Allyl Cations and Neutral Molecules (kcal / mol).

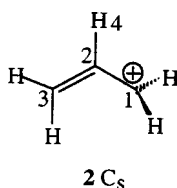
Molecule	E_π	E_σ	$E_\pi + E_\sigma$	E_{st}
1	-108.8	-164.0	-272.8	-1.6
5	-121.7	-151.1	-272.8	-6.0
3	-109.0	-160.7	-269.7	-5.9
6	-132.5	-139.2	-271.8	-9.7
38	-133.4	-134.1	-267.5	-3.4
21	-132.9	-137.5	-270.5	-7.8
7	-121.3	-146.6	-267.9	-9.1
15	-133.0	-136.4	-269.4	-12.8
12	-133.6	-134.4	-268.0	-15.8
17	-133.4	-129.0	-262.4	-17.8
9	-122.4	-152.7	-275.1	-5.6

(Continued)

TABLE I.
(continued)

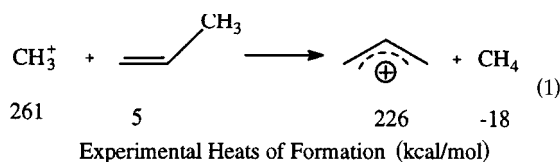
Molecule	E_{π}	E_{σ}	$E_{\pi}+E_{\sigma}$	E_{st}
	-122.2	-148.6	-270.7	-8.9
16 	-55.6	-73.8	-129.4	0.4
	-197.6	-497.5	-695.2	-2.6
	-181.2	-403.3	-584.5	-5.4

(CH₃—CH₃ to 2 CH₃). The results for ethene obtained by the latter method confirm the results obtained by the rotational barrier of ethene ($E_{\pi} = -69.6$ kcal/mol). Our force-field method gives—55.6 kcal/mol, which is somewhat lower.



The difference in the MMP2 π -energies of the allyl cation and ethene, 53.2 kcal/mol, can be attributed to the resonance stabilization of the allyl system. Although calculations on correlated *ab initio* levels show that a true rotational transition state of the unsubstituted allyl cation does not exist (the perpendicular structure **2** undergoes a 1,2 H-shift of H4 instead^{5,34}), RHF calculations gave rotational barriers over 30 kcal/mol, almost independent of the basis sets.^{12,35} Cobbi and Frenking reported that the perpendicular allyl cation is about 37.8 kcal/mol less stable than the planar minimum at MP2(full)/6-31G*//HF/6-31G*.³⁶ However, **2** is stabilized by hyperconjugation and by polarization of the π -electrons by the positive charge. The reduced C1—C2—H4 angle (RHF/6-31G*: 95.2°) shows the strong hyperconjugation effect; the π -electron densities (MP2(full)/6-31G*, C2: 1.164; C3: 0.815; and MMP2, C2: 1.226; C3: 0.774) document the polarization effect. Therefore,

the resonance energy of the allyl cation evidently must be higher than 37.8 kcal/mol. Our 53.2 kcal/mol estimate is not unreasonable, and is consistent with the stabilization energy of the allyl cation, relative to CH₃⁺, given by eq. (1), 59.7 kcal/mol at MP4sdtq/6-31G*//MP2(full)/6-31G* (58 kcal/mol from experimental data):



The small allyl C—C—C angle (117.6° at MP2(full)/6-31G*) has been attributed to the favorable 1-3 π -overlap of the π -orbitals of the two terminal allyl carbons.³⁷ The force-field method can evaluate this 1-3 π -interaction since the non-bonded resonance integrals can either be included or excluded. The 1-3 π -overlap stabilization of 9.5 kcal/mol, obtained as the difference,³⁸ is a significant contributor to the total MMP2 resonance energy of the allyl cation (53.2 kcal/mol). The importance of these 1-3 π -interactions also are shown by comparing the off-diagonal π -electron density matrix elements of the two terminal allyl carbons as a measure of π -bond orders obtained with MMP2 (0.473) and with MP2(full)/6-31G* (NLMO/NPA: 0.414). Figure 1 gives these off-diagonal π -electron density matrix elements as a measure of π -bond orders of the allyl cation at MMP2 and at MP2(full)/6-31G*.

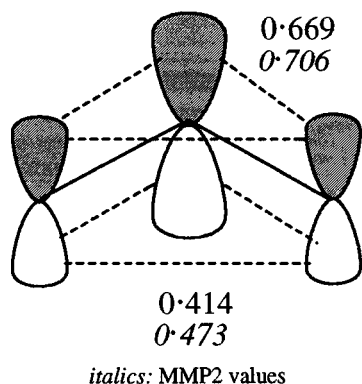


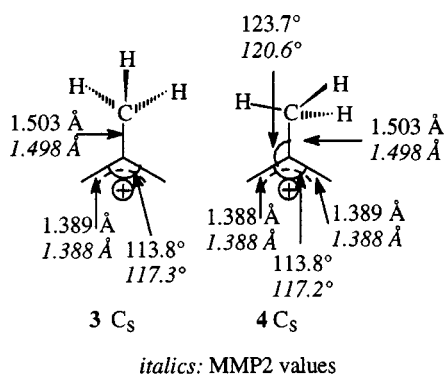
FIGURE 1. Off-diagonal π -electron density matrix elements as a measure of π -bond orders of the allyl cation at MMP2 and MP2(full)/6-31G* (correlated wave functions were used for the NLMO/NPA analysis).

This force field and *ab initio* evidence of strong 1-3 π -overlap in the allyl system confirm predictions more than 30 years old.^{6,39} Such 1-3 π -interactions in alkylated allyl cations are discussed in the last section.

Alkylated Open Chain Allyl Cations

2-METHYLALLYL CATION

The 2-methylallyl cation C_s symmetry with one perpendicular methy C—H bond (structure 3). Conformer 3 is favored over 4 by 0.01 kcal/mol according to MMP2 (MP4sdtq/6-31G**//MP2(full)/6-31G*: 0.02 kcal/mol; both conformers have almost identical zero point energies; 4 has one imaginary frequency), which indicates an almost free rotation of the methyl group:



The π -electron density of the central allyl carbon in 3 or 4 is slightly lower than that of the allyl cation. This is due to charge-charge repulsion of the σ -electrons of the C—H bonds with the π -elec-

tron of the central allyl carbon. Table II gives π -electron densities of allyl cations at MP2(full)/6-31G* and at MMP2.

The allyl cation angles in 3 and 4 are remarkably small (113.8° at MP2(full)/6-31G*), even smaller than the C—C—C angle (117.6°) in the parent allyl cation. The small angle in 3 and 4 implies even stronger 1-3 π -interaction due to the moderately larger π -electron densities of the terminal allyl carbons (corresponding MMP2 angles: allyl cation, 118.6° ; 2-methylallyl cation, 117.2°). The importance of strong 1-3 π -interactions in the 2-methylallyl cation was recognized by Olah and Comisarow three decades ago.⁶ This impressive insight is now confirmed by force-field and *ab initio* calculations.


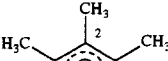
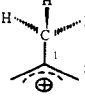
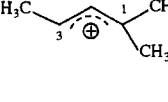

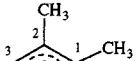
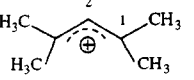
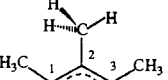
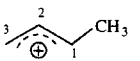
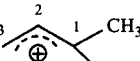
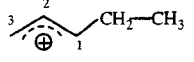
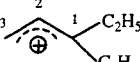
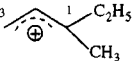
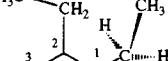
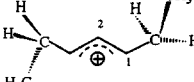


SUBSTITUTION OF TERMINAL ALLYL CARBONS BY ONE ALKYL GROUP

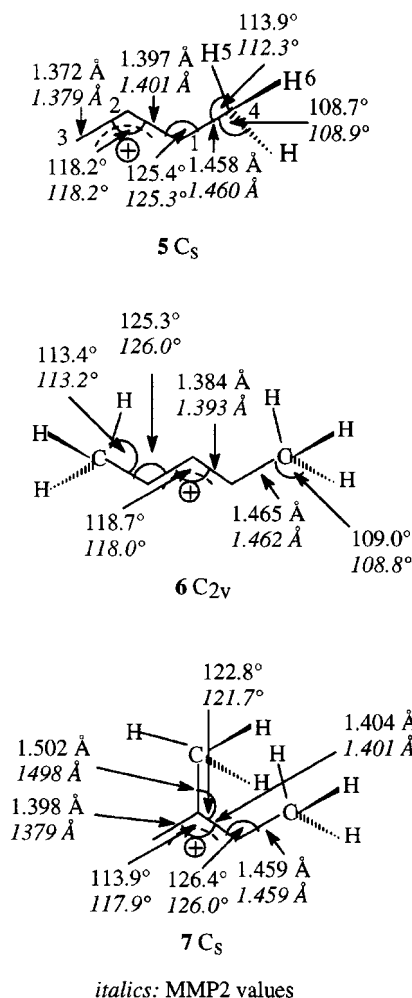
MMP2 and *ab initio* geometries of the 1-methylallyl cation 5, the $C_4H_7^+$ global minimum,⁴⁰ have been discussed elsewhere.³ The geometries and the π -electron densities obtained by these very different methods agree well. The most stable conformer, with an eclipsed conformation of the methyl group with the planar allyl system, is a consequence of a $\sigma-\sigma^*$ hyperconjugative interaction of the C—H bond parallel to the allyl system with an allyl C—C σ -bond. Analogous results were obtained with smaller basis sets several years ago;⁴¹ 5 also could be studied by IR spectroscopy.¹¹

The methyl groups attached to the terminal allyl carbons in the (*E,E*)-1,3-dimethylallyl cation⁴² 6, the (*E*)-1,2-dimethylallyl cation 7, and the (*E,E*)-1,2,3-trimethylallyl cation 8 (cf. Scheme 1 and Fig. 2) have conformations analogous to the methyl group in 5. The conformation of the central methyl group in 8 is similar to 3. The allyl carbon angles in these three cations are slightly reduced from 120° as a consequence of 1-3 π -interactions in the allyl system. Deviations of the allyl geometry from 1 are a result of the charge polarization of terminal allyl carbons due to hyperconjugation. The MP2(full)/6-31G* π -electron densities of the terminal allyl carbons are significantly higher than the corresponding MMP2 values as a consequence of electron donation from the hyperconjugating C—H bonds. This is not reproduced by MMP2, which does not include σ -electrons.

The 1-ethylallyl cation 9 prefers C_1 symmetry according to both MMP2 and MP2(full)/6-31G* optimizations (see Fig. 2). The out-of-plane ethyl C—C bond conformation is a consequence of

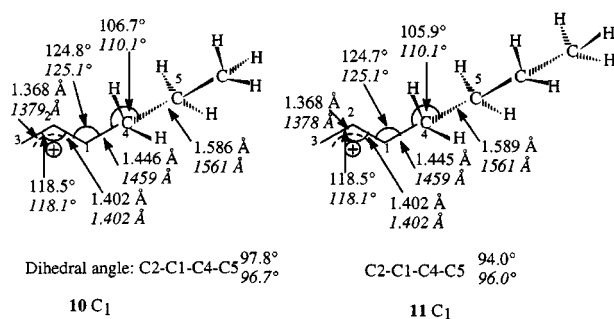
TABLE II.
 π -Electron Densities of Allyl Cations at MP2(full) / 6-31G* (MP2) and MMP2.

Cation	Atom	MP2	MMP2	Cation	Atom	MP2	MMP2
	1	0.453	0.473		1	0.454	0.426
	2	1.081	1.053		2	1.073	1.149
1				8			
	1	1.068	1.023		1	0.364	0.326
	2	0.462	0.488		2	1.142	1.236
3				22			
	1	0.497	0.410		1	0.308	0.294
	2	1.134	1.181		2	1.086	1.137
6				23			
	1	0.410	0.350		1	0.425	0.359
	2	1.160	1.300		2	1.124	1.278
28				29			
	1	0.373	0.366		1	0.304	0.288
	2	1.114	1.113		2	1.130	1.161
	3	0.508	0.521		3	0.559	0.551
5				21			
	1	0.354	0.361		1	0.276	0.272
	2	1.115	1.116		2	1.127	1.169
	3	0.526	0.524		3	0.590	0.560
9				27			
	1	0.290	0.279		1	0.365	0.376
	2	1.129	1.165		2	1.065	1.080
	3	0.574	0.555		3	0.556	0.545
25				14			
	1	0.431	0.407		1	0.238	0.096
	2	1.126	1.186		2	0.988	0.952
12				39			
	1	1.091	1.127				
	2	0.511	0.437				
38							



SCHEME 1.

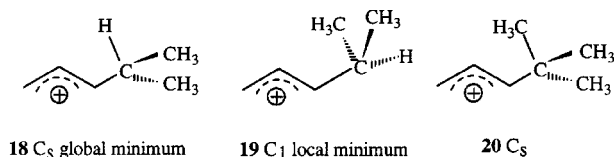
stronger hyperconjugative stabilization of the C—C bond. This hyperconjugation reduces the π -electron density at C1 compared to that in the 1-methylallyl cation (cf. Table II). The 1-(*E*)-*n*-propylallyl cation **10** and 1-(*E*)-*n*-butylallyl cation **11** are analogous.



The (*E,E*)-1,3-diethylallyl cation conformers **12** (cf. Fig. 2) and **13** (both are minima and have essentially identical energies), the (*E*)-1,2-diethylallyl cation **14** (cf. Fig. 2), the (*E,E*)-1-ethyl-3-methylallyl cation **15**, the (*E*)-1-ethyl-2-methylallyl cation **16**, and the (*E,E*)-1,3-diethyl-2-methylallyl cation **17** have analogous geometries. (Scheme 2) Cations with an alkyl group substituted to the central allyl carbon have small allyl C—C—C angles due to the strong 1-3 π -interactions (cf. 2-methylallyl cation). The dihedral angles of the terminal hyperconjugating ethyl groups with the allyl carbons approach 90° for cations with central allyl substituents due to steric interactions.

The MMP2 π -energies of **6**, **12**, and **15** (cf. Table I) illustrate the moderately better hyperconjugation ability of ethyl C—C bonds compared with C—H bonds.⁴³ The two allyl C—C bonds in **15** function similarly.

We found two minima for the 1-(*E*)-2-propylallyl cation (energy difference: MP4sdq/6-31G**//MP2(full)/6-31G*, 0.44 kcal/mol; MMP2, 1.05 kcal/mol). The C_s global minimum **18** has two symmetrical hyperconjugating ethyl C—C bonds and one C—H bond eclipsed with the allyl carbons. The minimum **19** has a dihedral angle of 102.6° between one hyperconjugating C—C bond and the allyl system (MMP2, 120°) and is closely related to the 1-ethylallyl cation. The only minimum for the 1-(*E*)-*t*-butylallyl cation **20** has C_s symmetry with one methyl group eclipsing the allyl system.



ALLYL CATIONS WITH GEMINAL ALKYL GROUPS

A detailed analysis of the 1,1-dimethylallyl cation **21**, also examined by Wiberg and coworkers,⁵ has been given previously.³ This was one of the key ions used in our development of MMP2 for cations.³ The *ab initio* geometry could only be reproduced by careful parameterization of torsional and van der Waals parameters in MMP2. The conformations of the methyl groups are typical for allyl cations with geminal methyl groups.

The (*E*)-1,3-trimethylallyl cation **22**, 1,1,2-trimethylallyl cation **23**, and the (*E*)-1,1,2,3-tetramethylallyl cation **24** (cf. Fig. 2) have geminal methyl group conformations closely related to **21**.

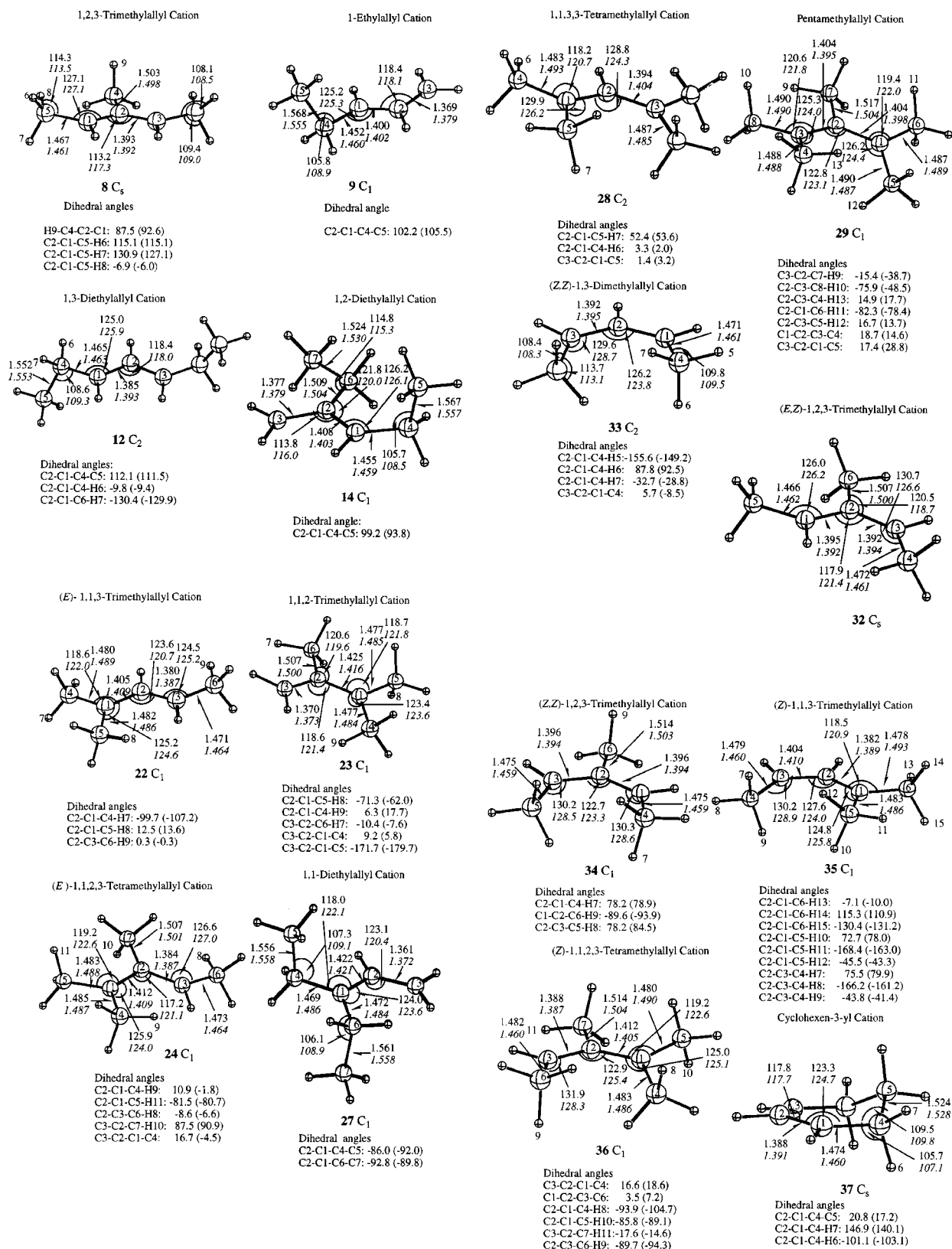
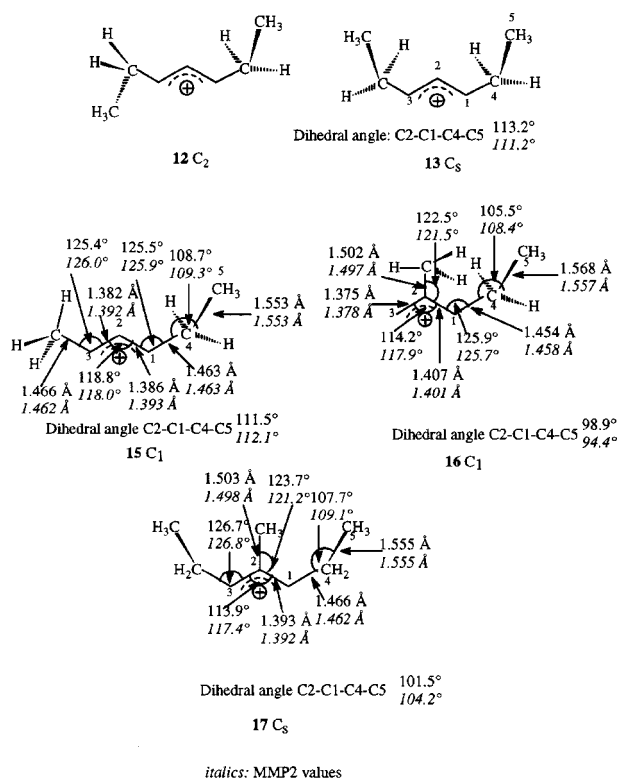


FIGURE 2. Geometry parameters of some alkylated allyl cations at MP2(full) / 6-31G* and MMP2. Bond lengths in angstroms; angles and dihedral angles in degrees. Italics indicate bond lengths and angles at MMP2; the MMP2 dihedral angles are given in parentheses.

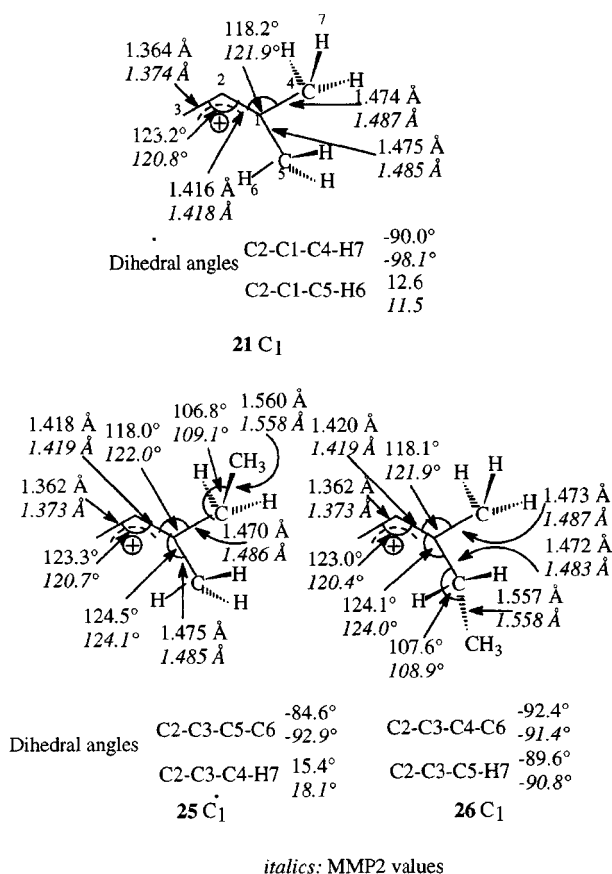


SCHEME 2.

Small variations are noted when the allyl system is distorted out of planarity; e.g., for all allyl cations with geminal alkyl substituents and an alkyl substituent at the central allyl carbon. The nonsymmetric substitution in 22, 23, and 24 lead to different allyl C—C bond lengths.

Allyl cations with at least one hyperconjugating C—C bond in the geminal alkyl substituents favor perpendicular conformations of the hyperconjugating C—C bonds toward the planar allyl system. The conformations of hyperconjugating methyl groups in geminal alkyl substituents are closely related to those in 21. The (*E*)-1-ethyl-1-methyl allyl cation 25 and (*Z*)-1-ethyl-1-methylallyl cation 26 (cf. Scheme 3) are typical examples. 25 is favored over 26 by 0.21 kcal/mol at MP4sdq/6-31G*//MP2(full)/6-31G* (MP2, 0.14 kcal/mol). The 1,1-diethylallyl cation 27 (cf. Fig. 2) has two ethyl C—C bonds with perpendicular conformations toward the allyl system.

The 1,1,3,3-tetramethylallyl cation 28 (cf. Fig. 2) has C_2 symmetry with almost staggered conformations of the (*Z*)-methyl groups, while the (*E*)-methyl groups eclipse the allyl system. MMP2 favors a C_{2v} structure with staggered conformations of the (*Z*)-methyl groups and eclipsed con-



SCHEME 3.

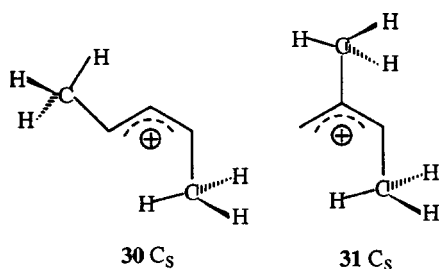
formations of the (*E*)-methyl groups with regard to the planar allyl system, but only by 0.07 kcal/mol over the C_2 structure (MP4sdq/6-31G*//MP2(full)/6-31G*: 0.01 kcal/mol in favor of the C_2 structure). The pentamethylallyl cation 29 (cf. Fig. 2) has C_1 symmetry; the remarkable distortion of the allyl system out of planarity results in almost eclipsed conformations of the (*Z*)-methyl groups with the allyl system. The geometries computed by the two different methods for this strained cation agree surprisingly well.

The MMP2 π -electron densities of 28 and 29 show satisfying agreement with the values at MP2(full)/6-31G* (cf. Table II). Again, MMP2 calculates significantly different π -electron densities for the allyl carbons, because the σ -donor effect of the hyperconjugating C—H bonds is not reproduced by MMP2.

(*E,Z*)-ISOMERISM IN THE ALLYL SYSTEM

The 1,3-dimethylallyl cation geometries of the various (*E,Z*)-isomers are typical. The (*E,Z*)-

isomer **30** favors eclipsed conformations of the two methyl groups with respect to the allyl system. The lower energy of the (*E,E*)-isomer over the (*E,Z*)-isomer is due to steric strain (torsional interactions are most important); the MMP2 π -energies of the two isomers are identical. Analogous results are found for the (*Z*)-1,2-dimethylallyl cation **31** (MMP2 preference of the (*E*)-isomer: 2.86 kcal/mol; MP4sdq/6-31G*//MP2(full)/6-31G*: 3.55 kcal/mol) and (*E,Z*)-1,2,3-trimethylallyl cation **32** (cf. Fig. 2). Table III shows that the energies relative to the most stable isomers at MMP2, at MP2(full)/6-31G*//MP2(full)/6-31G*, and at MP4sdq/6-31G*//MP2(full)/6-31G* agree well.



The allyl moiety of the (*Z,Z*)-1,3-dimethylallyl cation **33** (C_2 symmetry; cf. Fig. 2) is distorted slightly from planarity. Nevertheless, the MMP2 π -energy is almost identical with the (*E,E*)-isomer value. When hyperconjugative interactions were excluded from the SCF calculation, the π -energy of the planar (*E,E*)-isomer was favored by 1.0 kcal/mol. Hence, the (*Z,Z*)-isomer shows a slightly larger hyperconjugative stabilization than the (*E,E*)-isomer. The energy difference of the two isomers is steric [torsional contributions are most important; van der Waals interactions and angle strain favor the (*E,E*)-isomer by 2.5 kcal/mol].

Analogous conformations of the (*Z*)-methyl groups are favored in the (*Z,Z*)-1,2,3-trimethylallyl **34**, the (*Z*)-1,1,3-trimethylallyl **35**, and the (*Z*)-1,1,2,3-tetramethylallyl **36** cations. Geometry parameters of these cations are given in Figure 2. All cations with two (*Z*)-methyl substituents have allyl carbon angles that are significantly larger than 120° due to steric repulsion effects. The allyl system in **36** shows out-of-plane distortion. The MMP2 energy differences of the (*E,Z*)-isomers in the 1,2,3-trimethylallyl system agree well with those at MP4sdq/6-31G*//MP2(full)/6-31G* (cf. Table III). The corresponding MMP2 energy differences in the 1,1,3-trimethylallyl and 1,1,2,3-tetramethylallyl systems are reproduced exactly at MP4sdq/6-31G*//MP2(full)/6-31G* (1,1,3-trimethylallyl sys-

tem: 5.4 kcal/mol; 1,1,2,3-tetramethylallyl system: 5.2 kcal/mol).

MMP2 ISOMERIC ALLYL CATION ENERGY DIFFERENCES

The (*E,E*)-1,3-dimethylallyl cation **6** is computed to be more stable than the 1,1-dimethylallyl cation **21** (cf. Table III) due to electronic and steric effects. Although **21** has a slightly better π -energy, it is destabilized by the repulsions of the nearby methyl groups (the repulsion energy is added to the σ -energy; for a detailed description of the repulsive interactions in cations compare with ref. 3). The steric effect of the methyl groups also is apparent from comparisons of the steric energies of these carbocations. The (*E*)-1,2-dimethylallyl cation **7** is higher in energy than both **6** and **21** due to the small hyperconjugative stabilization of the central methyl group (the π -energy of **7** is less negative than that of **6** and **21**; cf. Table I). The better σ -energy of **7** compared with **6** and **21** (due to smaller methyl group repulsions) compensates for the π -energy differences.

Analogous interplay of steric and electronic effects are responsible for the different stabilities of the 1,1,3-trimethylallyl, 1,2,3-trimethylallyl, and 1,1,2-trimethylallyl cations (cf. Table III) as well as the 1,1,3,3-tetramethylallyl and 1,1,2,3-tetramethylallyl cations (energy differences of **24** vs. **28**: MMP2, 2.85 kcal/mol; MP4sdq/6-31G*//MP2(full)/6-31G*, 3.96 kcal/mol in favor of **28**).

HEATS OF FORMATIONS

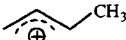
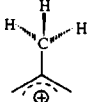

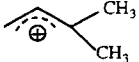
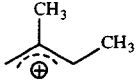
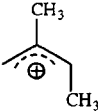
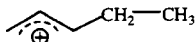


The MMP2 heats of formation of the alkylated allyl cations correspond well with experimental data.^{8,29} Table III shows that the relative energies of isomeric cations at MP2(full)/6-31G*//MP2(full)/6-31G* and at MP4/6-31G*//MP2(full)/6-31G* agree well with the experimental values. The heats of formation derived from Ibrahim and Schleyer's atom increments⁴⁴ agree, although the values for 2-alkylallyl cations tend to be somewhat too high.

Cyclic Allyl Cations

Unlike the cyclohexen-3-yl cation **37** (cf. Fig. 2), which behaves like its acyclic counterparts, cyclic allyl cations have long been considered to be special cases.⁴⁵ Solvolysis rates⁴⁶ as well as stability investigations in strong acids⁴⁷ suggest that the



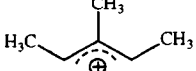
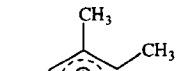
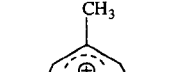
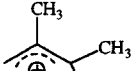
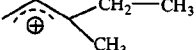
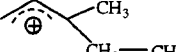
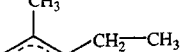
TABLE III.

Experimental [$\Delta H_f(\text{exp})$],^a MMP2 [$\Delta H_f(\text{MMP2})$], *Ab Initio* [$\Delta H_f(\text{MP4})$],^b and Atom Equivalent $\Delta H_f(\text{IS})$ ^c Heats of Formation, *Ab Initio* Energies^d (EMP2^e and EMP4^b), Number of Imaginary Frequencies (NIMAG), and Zero-Point Energies (ZPE; kcal / mol) of Allyl Cations, and Relative Energies ($E_{\text{rel}}2^{\text{e,f}}$ and $E_{\text{rel}}4^{\text{b,f}}$) of Isomeric Allyl Cations.

Cation	ΔH_f (exp)	ΔH_f (MMP2)	ΔH_f (MP4)	ΔH_f (IS)	$E_{\text{rel}}4$ $E_{\text{rel}}2$	NIMAG ZPE	EMP4 EMP2
	204	202.7		198.6	0.0	0	-155.80037
5 C _s					0.0	64.8	-155.75538
	211	211.0	214.2	213.5	10.2	0	-155.78439
3 C _s					10.1	64.7	-155.73921
	182	180.7	-	180.0	0.0	0	-195.00441
6 C _{2v}					0.0	83.6	-194.94901
	183	182.5	186.4	182.1	3.4	0	-194.99904
21 C ₁					3.6	83.5	-194.94323
	190	188.4	190.2	191.5	8.2	0	-194.99134
7 C _s					8.3	83.7	-194.93583
	-	192.3	193.7	195.1	11.7	0	-194.98569
31 C _s					8.5	83.5	-194.92973
	194	194.5	194.4	193.1	12.4	0	-194.98469
9 C ₁					12.4	84.3	-194.92922
	-	184.3	185.2	184.7	3.2	0	-194.99937
30 C _s					3.4	83.7	-194.94366
	-	190.4	191.0	191.4	9.0	0	-194.99013
33 C ₂					9.4	83.8	-194.93385

(Continued on next page)

TABLE III.
(continued)

Cation	ΔH_f (exp)	ΔH_f (MMP2)	ΔH_f (MP4)	ΔH_f (IS)	$E_{rel}4$ $E_{rel}2$	NIMAG ZPE	EMP4 EMP2
 22 C ₁	169	166.7	-	165.4	0.0 0.0	0 102.3	-234.17129 -234.13393
 35 C ₁	-	172.1	174.4	171.7	5.4 5.5	0 102.6	-234.16268 -234.12515
 8 C _s	170	172.3	174.2	175.3	5.2 4.5	0 102.4	-234.16230 -234.12674
 32 C _s	-	174.6	177.2	178.3	8.2 7.6	0 102.5	-234.15825 -234.12173
 34 C ₁	-	180.7	183.6	185.5	14.6 14.2	0 102.3	-234.14794 -234.11119
 23 C ₁	174	175.2	177.4	177.1	8.4 8.0	0 102.5	-234.15794 -234.12118
 25 C ₁	-	175.3	179.4	177.1	10.4 10.5	0 103.2	-234.15468 -234.11725
 26 C ₁	-	175.4	179.6	177.3	10.6 10.8	0 103.1	-234.15435 -234.11677
 16 C ₁	-	181.0	184.9	186.2	15.9 15.3	0 103.2	-234.14595 -234.10964

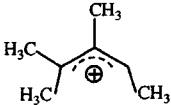

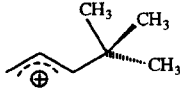
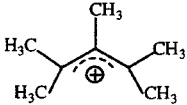
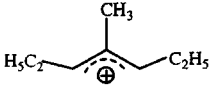



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TABLE III.
(continued)

Cation	ΔH_f (exp)	ΔH_f (MMP2)	ΔH_f (MP4)	ΔH_f (IS)	$E_{\text{rel}}4$ $E_{\text{rel}}2$	NIMAG ZPE	EMP4 EMP2
	-	173.9	176.5	174.8	7.5 7.5	0 103.0	-234.15933 -234.12196
15 C₁							
	-	187.2	189.4	188.0	20.4 20.5	0 103.6	-234.13879 -234.10137
10 C₁							
	-	185.4	187.2	187.5	18.2 17.9	0 103.3	-234.14232 -234.10547
18 C_s							
	-	186.4	187.6	188.4	18.6 18.2	0 103.3	-234.14163 -234.10492
19 C₁							
	157	156.1	-	158.4	0.0 0.0	0 121.4	-273.35674 -273.31400
28 C₂							
	-	167.2	171.3	172.4	14.3 14.5	0 122.8	-272.33393 -273.29097
27 C₁							
	-	174.9	177.7	181.3	20.7 20.4	0 122.6	-273.32397 -273.28154
14 C₁							
	-	166.5	168.7	168.6	11.7 12.1	0 122.5	-272.33808 -273.29478
12 C₂							
	-	158.9	161.0	163.5	4.0 3.4	0 121.4	-272.35043 -273.30861
24 C₁							

(Continued)

TABLE III.
(continued)

Cation	ΔH_f (exp)	ΔH_f (MMP2)	ΔH_f (MP4)	ΔH_f (IS)	$E_{rel}4$ $E_{rel}2$	NIMAG ZPE	EMP4 EMP2
 36 C ₁	-	164.1	166.2	169.5	9.2 8.7	0 121.6	-273.34215 -273.30016
 11 C ₁	-	181.3	181.9	182.4	24.9 25.5	0 122.8	-272.31704 -273.27336
 20 C _s	-	177.8	177.6	183.6	20.6 19.8	0 122.1	-273.32390 -273.28248
 29 C ₁	152	153.1	-	161.4	0.0 0.0	0 140.7	-312.52941 -312.48264
 17 C ₁	-	157.1	157.7	164.4	5.7 6.2	0 141.5	-312.52035 -312.47279
 37 C _s	191	189.0	-	188.4	- -	0 90.3	-233.00944 -232.95026
 38 C _{2v}	199	198.5	-	196.4	0.0 0.0	0 70.4	-193.82420 -193.77625
 39 C _{2v}	-	225.5	225.9	222.3	26.9 28.0	0 68.6	-193.78132 -193.73155

^aSee ref. 29.

^bAt MP4sdtq/6-31G*//MP2(full)/6-31G* for molecules with up to six carbons; for larger molecules at MP4sdtq/6-31G*//MP2(full)/6-31G*.

^cHeats of formation determined by Ibrahim and Schleyer's atom increments at HF/6-31G*//HF/6-31G*.

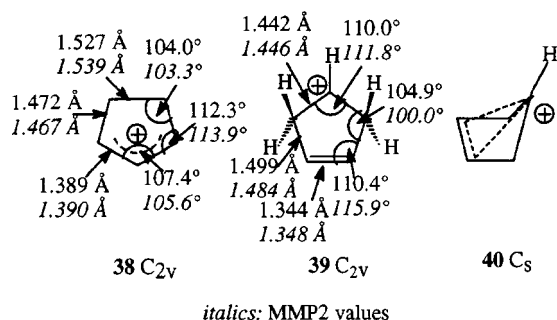
^d*Ab initio* energies are given in atomic units.

^eMP2(full)/6-31G*//MP2(full)/6-31G*.

^fValues in kilocalories per mole.

cyclopenten-3-yl cation **38** is specially stable. Strong hyperconjugative interactions of the $\text{CH}_2\text{—CH}_2$ group and a pseudoaromatic 6π character of the cyclopenten-3-yl cation were suggested to be responsible.⁴⁸ However, the gas phase hydride ion affinity of **38** is almost identical with that of its acyclic counterpart, the (*E,E*)-1,3-dimethylallyl cation.⁸ Comparison of the π -electron densities obtained at MMP2 and at MP2(full)/6-31G* (cf. Table II) showed no significant differences from those found for open chain allyl cations. The agreement of the MMP2 heat of formation of **38** (198.5 kcal/mol) with the experimental value (199 kcal/mol) indicates that the pseudoaromatic effect is unimportant. The geometry as well as the MMP2 π -energy (−133.4 kcal/mol; cf. Table I) of the cyclopenten-3-yl cation are closely related to the (*E,E*)-1,3-dimethylallyl cation (−132.5 kcal/mol; cf. Table I). The 1-3 π -overlap energy in **38** is found to be significantly larger than that in the (*E,E*)-1,3-dimethylallyl cation as a consequence of the small allyl C—C—C angle (MP2(full)/6-31G*: 107.4°; MMP2; 105.6°) in the five-membered ring (cf. Table IV). **38** has C_{2v} symmetry at MP2(full)/6-31G* and at MMP2 with four identical hyperconjugating C—H bonds. The MMP2 angle strain, 6.0 kcal/mol, evidently increases the steric energy (cf. Table I).

The cyclopenten-4-yl cation is interesting due to its structural relationship to the 7-norbornenyl cation.⁴⁵ What are the relative stabilities of a planar C_{2v} structure **39** and a nonplanar C_s structure **40**? Early solvolysis experiments were not able to detect double-bond participation,⁴⁷ but inappropriate nucleophilic solvents were used.⁵⁰ Stereochemical experiments by Lambert et al.⁵¹ and Kirmse et al.⁵² were consistent with a bridged intermediate **40** in solvolysis reactions. MP3/6-31G**//HF/6-31G* data favor **40** over **39** by 17.8 kcal/mol.⁵³



MMP2 optimization does not give **40**, because the force-field method has not been parameterized for such nonclassical structures. However, MMP2

single-point calculations on **40** (MP2(full)/6-31G* geometry) give a 24.8 kcal/mol lower SCF energy than that of **39**. The steric energy of **40** (which is minimized by MMP2) is 15.4 kcal/mol higher than that of **39**. This demonstrates that the MMP2 parameterization is not applicable to nonclassical structures.

The MMP2 π -electron densities of the two terminal allyl carbons in **38** and that of the charged carbon in **39** are too low. This results because the σ -donor effects of the hyperconjugating C—H bonds are not described by MMP2 (sum of the MP2(full)/6-31G* π -electron densities in **39**: 2.21). The energy difference of the two isomeric cyclopentenyl cations at MP4sdtq/6-31G*//MP2(full)/6-31G* (26.9 kcal/mol in favor of **37**) is reproduced excellently by MMP2 (27.0 kcal/mol).

HOMOCYCLOPROPENYL CATION— A HOMOAROMATIC 2π -ELECTRON SYSTEM?

Recent MP2(full)/6-311G** optimizations on the homocyclopropenyl cation²¹ **41** gave a puckered C_s geometry with a very small 1.744-Å distance between the two terminal allyl carbons. This cation was characterized by NMR spectroscopy about 30 years ago.⁵⁴ The experimental results focused interest on the homoaromatic 1-3 π -interaction, first suggested by Applequist and Roberts.²⁰ The crystal structure of the tetramethyl derivative, showing a nonplanar four-membered ring and a 1-3 distance of the two terminal allylic carbons of 1.78 Å, was attributed to the homoaromaticity of this cation.⁵⁵ Olah determined a ring inversion barrier of 8.4 ± 0.5 kcal/mol⁵⁶ and equated this value with the "homoaromatization energy."⁵⁷ The C_{2v} transition structure **42** has a larger 1-3 C—C distance. NLMO analysis²⁷ also indicated homoaromaticity.²⁰ Although MMP2 cation parameters have not yet been developed for three- and four-membered rings, the MMP2 SCF energies were obtained from single-point calculations on MP2(full)/6-311G** geometries of **41** and **42** with and without nonbonded resonance integrals. The differences give MMP2 estimates of 27.2 kcal/mol homoconjugation energy for **41** and 15.3 kcal/mol for **42** (cf. Table IV).

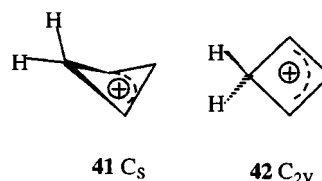

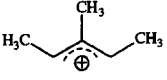
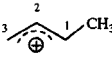
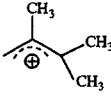
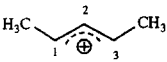


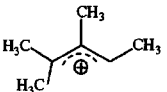
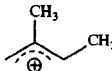


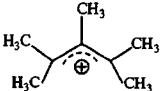
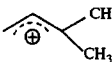
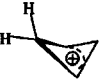
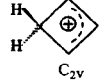


TABLE IV.

MMP2 Non-bonded Resonance Stabilization Energies (E_{nobo} ; kcal / mol) in Allyl Cations and 1-3 π -Density Matrix Elements of the Allyl, 1-Methylallyl, and 1,3-Dimethylallyl Cations at MMP2 [ED13(MMP2)] and at MP2(full) / 6-31G* [ED13(MP2)]^a.

Cation	E_{nobo}	ED13 (MMP2)	ED13 (MP2)	Cation	E_{nobo}
 1	9.5	0.473 ^b	0.414	 8	6.8
 5	7.9	0.437	0.382	 23	5.3
 6	6.5	0.410	0.364	 22	4.5
 38	9.3			 24	4.0
 7	7.8			 28	3.2
 3	9.8			 29	2.4
 21	5.2			 41 C_3	27.2
				 42 C_{2v}	15.3

^aCorrelated wave functions were used for the evaluation of the 1-3 π -density matrix elements in the NBO analysis.

^bThis value is identical with the MMP2 π -electron density of a terminal carbon in the allyl cation (cf. Table II) due to identical orbital coefficients of the terminal orbitals. The corresponding MP2(full) / 6-31G* values are different as a result of an electron delocalization in Rydberg orbitals.

The MMP2 aromatic stabilization energy of benzene [$E_{\pi}(\text{benzene}) - E_{\pi}(1,3,5\text{-hexatriene})$], -16.4 kcal/mol, is even smaller than the homoconjugation energy of **41**. This homoconjugation energy of **41** is significantly larger than that of **42** and the allyl cation due to larger terminal allyl carbon distances (allyl cation: 2.386 Å; **42**, C_{2v} : 1.977 Å).

The experimentally determined inversion barrier of 8.4 kcal/mol (MP4sdtq/6-311G**//MP2(full)/6-311G**: 9.41 kcal/mol) may be compared with the MMP2 difference (11.9 kcal/mol; cf. Table IV) in the homoaromaticity energies of **41** and **42**. We emphasize that the true homoconjugation energies are far larger than this ring inversion barrier. Surprisingly, even the allyl cation and **42** have large 1-3 π -interactions according to our force-field results. The total MMP2 homoconjugation energy of **41** (27.2 kcal/mol) is larger than the aromatic stabilization energy of benzene (-16.4 kcal/mol).

1-3 π -Overlap Effects in Alkylated Allyl Cations

Hyperconjugation of alkyl substituents in allyl systems leads to charge stabilization, to reduction of the π -electron densities of the trigonal carbons attached to the alkyl groups, and to reduction of π -electron density matrix elements. Therefore, hyperconjugation results in decreased 1-3 π -overlap effects. Table IV lists MMP2 allyl 1-3 π -overlap energies.

Comparison of the 1-3 π -density matrix elements of different alkylated allyl cations demonstrates the competing influence of hyperconjugation with nonbonded resonance. The MMP2 as well as the MP2(full)/6-31G* 1-3 π -density matrix elements, which represent the magnitude of 1,3 π -overlaps, reveal a parallel decrease in the allyl, the 1-methylallyl, and the 1,3-dimethylallyl cation series (cf. Table IV).

Alkyl substituents reduce 1-3 π -overlap effects both hyperconjugatively and sterically. The different stabilization energies in the cyclopenten-3-yl cation with its smaller allyl C—C—C angle and the (*E,E*)-1,3-dimethylallyl cation (both cations have almost identical π -electron densities due to their similar hyperconjugation; cf. Table II) as well as the strong 1-3 π -overlap energies in the homocyclopropenyl cations **41** and **42** demonstrate the bond angle influence impressively. Enlarged allyl C—C—C angles in (*Z*)-alkylallyl cations and allyl

out-of-plane distortions (cf. 1,1,2-trimethylallyl and pentamethylallyl cations) result in the small nonbonded resonance effects in highly alkylated allyl cations. Alkyl substitution at the central allyl carbon increases 1-3 π -overlap effects in allyl cations moderately due to a shift of π -electrons from the central to the terminal allyl carbons (cf. Table II).

Conclusions

The force field and *ab initio* geometries of alkylated allyl cations are similar. Therefore, MMP2 should provide good starting geometries for *ab initio* refinement. The MMP2 heats of formation agree well with experimental values as well as with data obtained from correlated *ab initio* evaluations. Relative energies of various allyl cation isomers at MMP2 are similar to the *ab initio* estimates.

The dissection of MMP2 carbocation energies into electronic and steric contributions or into σ - and π -energies allows the magnitude of resonance effects in delocalized cations to be evaluated.⁵⁸ The stabilization due to 1-3 π -overlap in the allyl system contributes significantly to the allyl resonance energy. Alkyl group hyperconjugation effects at terminal allyl carbons decrease these 1-3 π -interactions due to electronic and steric reasons.

Allyl cations (especially 2-alkyl-substituted derivatives) have significantly reduced allyl C—C—C angles as a result of attractive 1-3 π -overlap between the terminal carbons (2-methylallyl cation: 9.8 kcal/mol). Allyl cations with (*Z*)-alkyl substituents have widened allyl C—C—C angles due to steric repulsions.

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